(12) EUROPEAN PATENT APPLICATION

(21) Application number: 94202028.0

(51) Int. Cl.⁶: **C07D 201/16**

(22) Date of filing: 13.07.94

(71) Applicant: DSM N.V.
Het Overloon 1
NL-6411 TE Heerlen (NL)

(72) Inventor: Thijert, Marcellinus P.G.
Heggenhof 7
NL-6132 SP Sittard " (NL)
Inventor: van der Knaap, Theodorus A.
Heilig Kruisstraat 28
NL-6127 CC Born (NL)
Inventor: Haverkort, Johannes F.
412 Halifax Court
Martinez, Ga. 30907 (US)

(54) **Hydrogenation process for use purification of a water caprolactam mixture.**

(57) Process for the purification of ε-caprolactam, which involves hydrogenation of a water-ε-caprolactam mixture with hydrogen of the mixture in the presence of a heterogeneous hydrogenation catalyst, wherein first the ε-caprolactam-water mixture is contacted with gaseous hydrogen, upon which hydrogen dissolves in the ε-caprolactam-water mixture, and subsequently this hydrogen-containing mixture is contacted with the hydrogenation catalyst and that 90-100% of the hydrogen present during hydrogenation has been dissolved in the water-ε-caprolactam mixture.

EP 0 635 487 A1

The invention relates to a process for the purification of ε-caprolactam which involves hydrogenation of a water-ε-caprolactam mixture with hydrogen in the presence of a heterogeneous hydrogenation catalyst.

To obtain ε-caprolactam of the purity required for polymerization to nylon 6, impure ε-caprolactam, prepared by for example Beckmann rearrangement of cyclohexanone oxime, is subjected to a number of

5 purification steps. One of these purification steps is the hydrogenation, as referred to here, of a mixture consisting substantially of water and ε-caprolactam and some unsaturated impurities. Hydrogenation of water-ε-caprolactam mixtures are carried out to hydrogenate these unsaturated compounds present in the impure ε-caprolactam. The presence of these unsaturated compounds are disadvantageous because they can impair the physical-mechanical properties of the nylon-6 made by polymerizing ε-caprolactam. The

10 saturated compounds formed by hydrogenation do not adversely influence these physical-mechanical properties of the nylon-6 and moreover these compounds are more easily removed in for example a distillation step following the hydrogenation step.

Such a process is described in EP-A-411455. EP-A-411455 describes the purification, in a three-phase system (gas, liquid, solid), of a 75-95 wt.% aqueous ε-caprolactam mixture in which the water-ε-caprolactam

15 mixture and gaseous hydrogen are passed from the bottom upwards through a fixed bed consisting of a supported palladium or nickel catalyst.

In this known method the amount of hydrogen fed to the reactor is relatively large, compared with the amount of hydrogen consumed during the reaction. The residual amount of hydrogen is incinerated or recirculated to the hydrogenation reaction. In the latter case the hydrogen is passed through a compressor

20 to ensure that it has the correct pressure when it is returned to the reactor. A drawback of this process is that large amounts of hydrogen have to be processed which will result in more safety measures, because of the nature of hydrogen. A further drawback of this method is that the system requires a relatively large compressor to keep a large amount of hydrogen in circulation. When the residual amount of hydrogen is incinerated economics prove to be unattractive because the burning value of hydrogen is less than the

25 hydrogen cost price.

The object of the invention is to provide a more efficient and more safe process for the purification of ε-caprolactam.

This object is achieved in that first the ε-caprolactam-water mixture is contacted with gaseous hydrogen, upon which hydrogen dissolves in the ε-caprolactam-water mixture and subsequently this hydrogen-

30 containing mixture is contacted with the hydrogenation catalyst and that 90-100% of the hydrogen present during hydrogenation has been dissolved in the water-ε-caprolactam mixture. Preferably, 98-100% of the hydrogen has been dissolved in the water-ε-caprolactam mixture. When for example 98% of the hydrogen is dissolved in the mixture the remaining 2% of the hydrogen is in the gaseous phase.

In the process disclosed herein, a mixture comprised substantially of water, ε-caprolactam, and

35 unsaturated impurities can be purified to yield ε-caprolactam of the same purity as the ε-caprolactam purified by the process disclosed in EP-A-411,455, but without a large amount of unreacted hydrogen remaining after hydrogenation. This allows for use of simpler reactor equipment. Furthermore there is no need to install equipment for recirculating unreacted hydrogen or equipment for incinerating hydrogen.

In the process disclosed herein, the residence time of the liquid in the hydrogenation reactor can be

40 shortened substantially compared to the process disclosed in EP-A-411455. A short residence time is advantageous because either a smaller reactor volume can be used while the reactor load remains the same, or a higher reactor load can be used while using the same reactor volume.

According to the process of the invention disclosed herein, very little hydrogen is present in gaseous form in the hydrogenation reactor. In contrast to the conventional thinking revealed in prior art, a quantity of

45 hydrogen that can dissolve in the reaction mixture under the reaction conditions is sufficient to purify the ε-caprolactam. Hydrogen is a difficult gas to compress, due to its small molecular size, and use of less hydrogen also results in improved safety.

The heterogeneous catalyst can be contacted with the hydrogen-containing reaction mixture in various ways. Hydrogenation may for instance take place in a stirred tank reactor in which the catalyst particles are

50 suspended in the mixture to be purified (slurry phase process). A drawback of the slurry phase process is that the catalyst particles and the purified mixture must be separated in an additional process step after the hydrogenation reaction. Such a separation step, for instance by means of filtration, is cumbersome. Therefore, the hydrogenation is more preferably effected in a fixed-bed reactor with the catalyst being fixed in the reactor, so that the additional step for separation of the catalyst and reaction mixture can be

55 dispensed with.

When the ε-caprolactam-water mixture is contacted with the gaseous hydrogen the mixture will become completely or partially saturated with hydrogen.

The degree to which the reaction mixture generally is saturated with hydrogen is between 50-100%. Preferably, the degree of saturation of the reaction mixture is between 80-100%. The amount of hydrogen in the reaction mixture will depend on temperature, pressure and contact time of the hydrogen and the mixture when dissolving the gaseous hydrogen. With the degree of saturation is meant the percentage of the maximum amount of hydrogen which can dissolve in the mixture at a certain temperature and pressure. By adding more than the maximum amount of hydrogen a gaseous phase will be present. It has been found that the solubility of hydrogen in the water-ε-caprolactammixture is almost comparable with the solubility of hydrogen in pure water for the mixtures which can be treated with the process according to the invention (thus irrespective of the ε-caprolactam concentration).

The ε-caprolactam weight percentage in the water-ε-caprolactam mixture (excluding hydrogen) may be between 10 and 95 wt.%. A low ε-caprolactam content is advantageous as it allows of dissolution of a larger amount of hydrogen. However, a very low ε-caprolactam content is not advantageous, for in that case a large quantity of inert water circulates and evaporates. The ε-caprolactam content will therefore preferably be higher than 30 wt.%. Preferably, the ε-caprolactam content is lower than 50 wt.%, and most preferably it is below 40 wt.%.

The hydrogenation temperature is generally between 20 and 160°C. As a rule a not too low temperature will be chosen, for at a low temperature the reaction time is longer. The temperature is as a rule not too high because high temperatures have a negative influence on the ε-caprolactam quality. The temperature therefore preferably is between 70 and 130°C, and most preferably between 80 and 100°C.

The hydrogenation pressure may be between 0.1 and 15 MPa. High pressures are advantageous as they allow dissolution of a larger quantity of hydrogen in the water-ε-caprolactam mixture. Since the impurity content is normally not so high as to necessitate a large quantity of hydrogen, an excessively high pressure is not needed. Very high pressures further have the drawback that expensive process equipment is needed. As a rule, therefore, the pressure is between 0.3 and 5 MPa.

The process according to the invention can be performed batchwise. Preferably the process is performed as a continuous process.

The hydrogenation residence time or contact time depends on the method that is chosen for contacting the heterogeneous catalyst with the hydrogen-containing water-ε-caprolactam mixture. If a reactor is chosen in which the catalyst is fixed in the reactor (fixed-bed reactor), the residence time in a continuous process is generally more than 10 seconds, and in particular more than 30 seconds, and in general the residence time is less than 10 minutes and in particular less than 7 minutes.

The amount of hydrogen used per amount of ε-caprolactam to be purified will depend on the temperature, pressure, degree of saturation and solubility of hydrogen and the degree of impurities to be hydrogenated.

Without recycling, if applied, of non-converted hydrogen the hydrogen volume quantity per weight quantity of caprolactam to be purified (excluding water) as a rule is between 0.001 and 2 Nm^3/tonne lactam $(5 . 10^{-5} - 1.0 . 10^{-2}$ mol H_2 per mol ε-caprolactam) and preferably between 0.1 and 1 Nm^3/tonne lactam $(5 . 10^{-4} - 5 . 10^{-3}$ mol H_2 per mol ε-caprolactam).

Dissolution of the hydrogen in the water-ε-caprolactam mixture can be effected by any process that is known to one skilled in the art. Preferably, the mixture is contacted with hydrogen in a mixer in which a constant hydrogen pressure is maintained. Intensive contact between the hydrogen and the mixture will ensure that the hydrogen dissolves in the mixture. Such a process is preferably carried out continuously. The hydrogen-containing mixture is subsequently contacted with the hydrogenation catalyst for example in a separate reactor.

As a rule the pressure and the temperature during hydrogen dissolution in the water-ε-caprolactam mixture are virtually the same as the pressure and temperature that is maintained in the hydrogenation reactor. Depending on specific conditions, for instance in the case of heat recovery, there may be a somewhat larger difference between the pressure and temperature at which hydrogen dissolution takes place and the hydrogenation pressure and temperature.

The hydrogenation catalysts may be any known heterogeneous hydrogenation catalyst. Examples of such catalysts are ruthenium on aluminium oxide, rhodium on aluminium oxide, platinum on carbon, palladium on carbon, Raney nickel, nickel on silica and nickel on aluminium oxide. Preferably, use is made of nickel-containing catalysts.

Suitable nickel catalysts as a rule have a nickel content between 5 and 80 wt.%, relative to the metal and the support. Besides nickel the catalyst may contain some activators such as Zr, Mn, Cu or Cr. The activator content is generally between 1 and 20 wt.%.

If palladium-containing heterogeneous catalysts are used, the palladium content will generally be between 0.01 and 10 wt.%.

If a fixed-bed reactor is used, catalysts are employed in which an active metal is on the external surface of a support. Such catalysts can be prepared using the method in which a pre-formed support (for instance pellets, spheres or ribbons) is contacted with an aqueous solution of a metal salt, for example the metal nitrate, dried, and subsequently calcined.

The size of the pre-formed support that is chosen will be as small as is possible without the pressure drop across the fixed bed becoming unacceptable. For example the average particle diameter of pellets is usually between 1 and 5 mm.

In case freshly prepared catalyst is used the catalyst shall often have to be activated in order to reduce the metal oxides to catalytically active free metal.

Catalyst activation can be effected in any known manner. For example hydrogen can be used to reduce the metal oxides. In Example 3 of EP-A-411455, for example, the catalyst is activated by passing gaseous hydrogen over the catalyst for 8 hours while increasing the temperature stepwise from 80 to 200°C. This known process for activating the hydrogenation catalyst is however disadvantageous because large quantities of valuable hydrogen are consumed by the process. It has now been found that activation can be carried out at a temperature of 70-100°C if the catalyst to be activated is contacted with water in which hydrogen is dissolved. The activation pressure may be between 0.1 and 10 MPa. In comparison with the activation as described in EP-A-411455 the above-mentioned activation is advantageous because: (1) catalyst activation is carried out at a lower (maximum) temperature, (2) catalyst activation is carried out in situ so that no extra facilities are needed to pass gaseous hydrogen to the catalyst bed especially for the activation and (3) no excessive usage of hydrogen is necessary.

In order to prepare the aqueous solution of hydrogen needed for catalyst activation, hydrogen can be dissolved in water in the same way as previously described for dissolution of hydrogen in the mixture of water, ε-caprolactam, and unsaturated impurities. Concerning the catalyst activation process, the reaction conditions used to dissolve hydrogen in water are virtually the same as the reaction conditions, such as temperature and pressure, used to activate the catalyst.

Activation of the catalyst can also be carried out using the previously described mixture of water, ε-caprolactam, hydrogen, and unsaturated impurities. This mixture can be contacted with the hydrogenation catalyst in the same manner as in the purification described above at a temperature between 70-100°C. The advantage of using this mixture directly is that catalyst activation can be carried out, in situ, when the purification is started without any adaptation of the process operation. Under normal operating conditions, applying a hydrogen containing water-ε-caprolactam mixture as described above, 12 to 48 hours are sufficient to activate the catalyst to a level at which high-purity ε-caprolactam can be obtained.

The ε-caprolactam to be purified can be prepared by the Beckmann rearrangement in oleum as described in DE-A-2508247 or other preparation processes, such as for instance the rearrangement reaction in the presence of an acid ion exchanger as described in GB-A-1342550. Caprolactam obtained by depolymerization of nylon 6, as described in US-A-5169870, can also be purified advantageously using the process according to the invention.

In practice the purity of ε-caprolactam obtained by purification of a mixture of water-ε-caprolactam by evaporation and distillation (as is disclosed in US-A-4563308) is expressed by the permanganate absorption number (PAN). The PAN is determined in accordance with ISO 8660. ε-Caprolactam obtained from an unpurified mixture of water, ε-caprolactam and unsaturated generally has a PAN ranging from 4 to 6. The PAN of ε-caprolactam obtained from a water-ε-caprolactam mixture that has been purified according to the invention disclosed herein is lower than 4 and generally higher than 1. Preferably, the PAN is lower than 3.

Another way of expressing the purity of the ε-caprolactam eventually obtained is by means of the PM number (permanganate number). Like PAN, the PM number is a measure of the oxidizability. A higher PM number means that a smaller amount of oxidizable impurities is present. Yet another way of expressing the purity is by means of the amount of unsaturated compounds (in ppm).

The 'permanganate number' (= PM number) is defined as the number of seconds elapsing after the addition of 1.00 ml of potassium permanganate 0.0020 Mol/l to 100 ml of caprolactam solution (3.00 g/100 ml) of 293 K (= 20°C) until the moment at which the colour of this solution becomes equal to the colour of a standard solution. The standard solution consists of 3000 mg of cobaltnitrate ($Co(NO_3)_2$. 6 H_2O) and 12 mg of potassium dichromate in 1 l water. The PN number may only be used for comparison purposes of the Experiments and Examples as described below.

The invention will be elucidated by means of the following non-limiting examples.

Examples I-III

The aqueous caprolactam in these examples was obtained by Beckmann rearrangement of cyclohex-anone oxime in oleum and neutralization with ammonia, benzene extraction followed by re-extraction with
5 water: The mixture after neutralization was introduced into a 1.0 l stirred reactor together with benzene (3 g mixture/1.5 g benzene). The resulting mixture was stirred for 15 minutes and subsequently two phases, a "water phase" and a "benzene phase" formed, which were separated by phase separation.

The water phase was again introduced into the reaction together with fresh benzene (5.0 g ben-zene/10.0 g water-phase). The mixture was again stirred for 15 minutes and subsequently separated into
10 two phases. This extraction step with benzene was repeated two additional times. The resulting "four benzene phases" were mixed with fresh water (25 g/100 g benzene phase). This mixture was stirred for 15 minutes and subsequently separated into two phases.

This water extraction was repeated two additional times. The resulting water phases from the benzene extraction and the water phases obtained from the water extraction were mixed together. This yielded a 35
15 wt.% caprolactam solution in water. A process according to the invention was used to treat this mixture further by saturating the solution with hydrogen in step a) and passing the solution over a hydrogenation catalyst in step b).

a) In a continuously operated, stirred tank (diameter 100 mm, filling level 100 mm and provided with a heating jacket) the 35 wt.% caprolactam solution in water was fully pre-saturated in a mixer in which a
20 constant hydrogen pressure of 0.6 MPa was maintained and pH 7 the temperature stated in Table 1.

b) Through a vertical tubular reactor (diameter 34 mm, filling level 27 mm, heating jacket) filled with 25 ml (20 grammes) nickel catalyst (ca. 50 wt.% nickel (oxide) on alumina/silica, diameter 3 mm, length 8 mm) a continuous flow was established of the hydrogen-saturated caprolactam solution. The flow passed through the catalyst bed from the bottom upwards at the same temperature as in Table 1 and at 6 bar
25 and pH 7 (for flow rates see Table 1). In situ catalyst activation took place.

After 12 hours the first sample was taken. The sample was further processed by means of evaporation and distillation as described in Example 1 of US-A-4563308, after which the PAN and the PM number as well as the total quantity of compounds to be hydrogenated were determined. The results are given in Tables 1 and 2. Hydrogenation was continued for 10 days. The purification of the final product did not
30 deviate significantly from the results listed in Table 2. This proved that catalyst activation had been completed after 12 hours.

TABLE 1

Example	Temp. (°C)	Liquid flow (g/h) 1)	H_2 consumption (nl/h) 2)	Residence time (sec.)
I	90	250	0.03	145
II	85	500	0.03	75
III	100	250	0.022	145

1) g/h = gramme of water/ε-caprolactam/hydrogen mixture per hour
2) nl/h = normal litre of hydrogen per hour consumed in the stirred tank and is equal to the amount of H_2 flowing through the reactor.

The water-ε-caprolactam mixture with the dissolved hydrogen was in all the Examples I-III a homogeneous mixture (no gas phase present).

The amount of unsaturated compounds in the caprolactam solution fed to and discharged from the hydrogenation was determined; the results are presented in Table 2.

TABLE 2

No.	PAN 1)	PM (sec.) 2)	ppm in feed	ppm in discharge
I	1.8	39,000	10	< 1
II	2.1	35,000	5	< 1
III	1.9	45,000	10	< 1

1) measured according to ISO 8660

2) PM number. A higher number indicates that a lower amount of oxidizable impurities is present.

Comparative Experiment A

Without further purification (hydrogenation) the 35 wt.% caprolactam mixture in water of Example I was evaporated and distilled in the same way as in Example I. The caprolactam proved to have a PAN of 5 and a PM of 12,000 sec.

Comparative Experiments B-E

The 35 wt/% aqueous caprolactam solution used in these experiments is the same as that used in Example I (after extraction). In this series of experiments use was made of a bubble column according to EP-A-411455. Contrary to Examples I-III, a large quantity of gaseous hydrogen was present during hydrogenation.

a) A vertical tubular reactor (diameter 34 mm, filling level 27 cm, jacket heating) was filled with 250 ml already activated (160 g) nickel catalyst (ca. 50 wt.% nickel/nickel oxide on alumina, for diameter (d) see Table 3, length 5 to 8 mm). Hydrogenation was effected by pumping gaseous hydrogen (25 nl/h) and the caprolactam solution in water (35 wt.% caprolactam) for 90 minutes through the bed from the bottom upwards, this taking place at 90°C, 0.6 MPa and pH 7.

The other conditions are listed in Table 3. The concentration of unsaturated compounds was determined both in the feed and in the discharge flow.

TABLE 3

Exp.	Temp. (°C)	Residence time (min.)	Liquid flow (g/h)	H₂ flow (nl/h)	d_{cat} (mm)
B	90	18	250	25	1.6
C	90	18	250	25	3.2
D	90	9	500	25	1.6
E	90	9	500	25	3.2

Upgrading of the caprolactam solution in water by evaporation and distillation (as in Example I) resulted in the final product quality as indicated in Table 4.

TABLE 4

Exp.	PAN	PM	ppm in feed	ppm in discharge
B	1.9	35,000	11	< 1
C	2.3	35,000	11	< 1
D	2.3	37,000	11	< 1
E	3.0	27,000	11	2

The results show that use of a packed bubble column at the same load and a longer residence time leads to comparable purities, with hydrogen consumption being many times higher.

Claims

1. Process for the purification of ϵ-caprolactam, which involves hydrogenation of a water-ϵ-caprolactam mixture with hydrogen of the mixture in the presence of a heterogeneous hydrogenation catalyst, characterized in that first the ϵ-caprolactam-water mixture is contacted with gaseous hydrogen, upon which hydrogen dissolves in the ϵ-caprolactam-water mixture, and subsequently this hydrogen-containing mixture is contacted with the hydrogenation catalyst and that 90-100% of the hydrogen present during hydrogenation has been dissolved in the water-ϵ-caprolactam mixture.

2. Process according to claim 1, characterized in that 98-100% of the hydrogen has been dissolved in the water-ϵ-caprolactam mixture.

3. Process according to any one of claims 1-2, characterized in that the molar quantity of hydrogen per mol of ϵ-caprolactam to be purified is between $5 . 10^{-4}$ and $5 . 10^{-3}$ mol H_2 per mol ϵ-caprolactam.

4. Process according to any one of claims 1-3, characterized in that the ϵ-caprolactam concentration is between 10 and 95 wt.%.

5. Process according to claim 4, characterized in that the ϵ-caprolactam concentration is between 10 and 40 wt.%.

6. Process according to any one of claims 1-5, characterized in that the temperature is between 70 and 130°C.

7. Process according claim 6, characterized in that the temperature is between 80 and 100°C.

8. Process according to any one of claims 1-7, characterized in that the hydrogenation is carried out in a fixed bed.

9. Process according to claim 8, characterized in that the hydrogenation is carried out continuously and the residence time is between 10 seconds and 10 minutes.

10. Process according to any one of claims 1-9, characterized in that the the activation of the catalyst is carried out in situ by contacting the hydrogen containing water-ϵ-caprolactam with the hydrogenation catalyst at a temperature of 70-100°C.

11. Process as substantially described in the description and the examples.

7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP-A-0 411 455 (BASF) * the whole document *	1-11	C07D201/16
A	FR-A-1 388 442 (TOYO RAYON KABUSHIKI KAISHA)	1-11	
A	EP-A-0 138 241 (STAMICARBON (DSM SUBS.)) * example 1 *	1-11	
A	FR-A-1 337 527 (SNIA VISCOSA) 27 August 1962 * page 3 *	1-11	
A	FR-A-1 332 193 (BASF) 25 June 1962 * the whole document * * page 2, line 14 - line 18 * * page 3, line 46 - line 51 * * examples 17,21,22 *	1-11	

	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 October 1994	Kissler, B